



217/782-6761

Refer to: 04180801 -- Douglas County  
Tuscola/Cabot Corporation

May 14, 1984

Cabot Corporation  
P. O. Box 188  
Tuscola, Illinois 61953

Attention: Mr. Randy Bergeson  
Process/Project Engineer

Dear Mr. Bergeson:

As I mentioned earlier last week, an assessment of the practice of disposing acidic wastes into carbonate formations was recently provided by USEPA, Region V. I am sending a copy of these reports for your company's consideration.

Should you have any questions or comments regarding the reports, submit them in writing to:

U. S. Environmental Protection Agency  
Region V  
230 South Dearborn Street  
Chicago, Illinois 60604

Attention: Robert J. Hilton, Chief  
Ground Water Section

Additionally, please send a copy to the IEPA of relevant correspondence for our evaluation.

In regard to your question of May 7, 1984, the requirements and implication of Sec. 730.113(b)(4), Subtitle G: Waste Disposal, Title 35: Environmental Protection are currently under review. As soon as a state-wide approach is formulated, we shall inform you of necessary action.

EPA Region 5 Records Ctr.



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Thank you for your consideration. If you have any questions or if we can be of assistance, please do not hesitate to contact us.

Sincerely,

A handwritten signature in black ink, appearing to read "John D. Student". The signature is fluid and cursive, with a large, stylized "J" and "S".

John D. Student  
Compliance Sub-Unit  
Compliance Monitoring Section  
Division of Land Pollution Control

JDS:tk/27

Enclosures

cc: Mark Haney  
Monte Nienkerk  
Central Region  
USEPA, Region V  
Division File ✓

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
REGION V

DATE: March 28, 1984

SUBJECT: Disposal of Acidic Waste in Cavernous/Fractured  
Carbonate Formations

FROM: Robert J. Hilton, Chief  
Ground Water Section

TO: Tom Belk, Chief  
Ground Water Branch (WH-550)

Since the submission of the report on the assessment of Class I hazardous waste disposal wells in Region V in October 1983, we have obtained more detailed information from State files, pertinent to the safe operation of certain Class I wells. A detailed review of the operational history of an Illinois injection well which disposes of acidic wastes into cavernous carbonate formations has revealed a serious problem. Waste disposal by this method is a common practice in Illinois. During August 1975, the disposal well at the Cabot Corporation's facility in Tuscola, Illinois, failed to accept fluid and subsequently erupted into a 10 foot geyser spewing previously emplaced effluent at approximately 250 gpm until it was capped two days later. The tubing was ejected from the well and the casing damaged. (The incident is discussed in greater detail in the attachment).

It is our belief that the pressurization of the disposal zone by carbon dioxide generated in situ by the chemical reaction between the acidic wastes and the carbonate formation caused the effluent backflow. The occurrence of similar well blowouts in other facilities disposing acid wastes into carbonate formations cannot be ruled out unless the underlying cause viz. the chemical interaction of acid and disposal formation leading to the generation of carbon dioxide is eliminated. This can be done by the simple neutralization of the acid with alkali or limestone or by other suitable methods prior to deep well disposal. A less desirable and possibly less practical alternative would be to render the waste essentially non-reactive by dilution with fresh water. Also, it does not appear that the cost of treating the acid waste to make it permanently inert would be overly burdensome to the operator, especially considering the resulting safety of the well operation.

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Acid Waste Disposal in Cavernous/  
Fractured Carbonate Formations

Introduction

The disposal of acid wastes from manufacturing plants into fractured or cavernous dolomite formations has been a major element of industrial waste management in Illinois since 1966. The reported success of the operation of a 5000 feet deep disposal well completed in the cavernous Potosi dolomite formation by the Cabot Corporation, Tuscola, IL. has prompted other operators in the State (U.S.I., Tuscola and Allied Chemical Company, Danville, IL.) to construct and operate similar facilities at their own plant sites. The documented history of the original Cabot well, however, appears to cast some doubt regarding the safety of these operations: The disposal zone appears to have been pressurized by the carbon dioxide produced by the chemical interaction of the waste hydrochloric acid and the dolomite formation, as a result of which the well had a blow-out in August 1975 and subsequently erupted as a 10 foot geyser spewing emplaced waste at a steady rate, until it was capped 2 days later.

This report attempts to put into scientific/engineering perspective the limitations of this type of waste disposal by well injection, and possible criteria for the safe disposal of wastes into cavernous dolomites in terms of the Cabot well experience and possible causes of the reported failure of the well.

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open holding ponds at the facility. The two waste acid streams were at concentrations of about 30% and 2% acid respectively. Other wastes injected into the deep well included an etching solution waste from the Donnelly Co., Mattoon, and "starchy wastes" from the Staley Starch Co., Decatur.

#### Well Blowout in August 1975

It is apparent from the State EPA records, that the well had operational problems ("surface water incidents") in April 1973, April 1975 and again in August 1975, causing surface pollution and fish-kills. The most serious of these occurred in August 1975, after an "unusual amount of strong acid was injected into the well intermittently for several weeks." The failure of the well to accept fluid led the operator to believe that there was solids build-up in the tubing. To clear this "blockage" a strong solution of calcium chloride was injected into the well at a high rate. This resulted in the rupture of the tubing. Subsequently, the pressure at the wellhead rose to above 450 psi, and the well erupted twice, before it appeared to have died. During the first eruption (blowout), a joint of the tubing was ejected through the head of the casing. During the work over of the well, fresh water from the fire hydrant system was allowed to flow down the well at an initial rate of 50 gpm, and 25 gpm two days later. The well erupted again on August 24, 1975, and continued to back-flow fluids as a 10 foot gusher discharging at an estimated steady rate of about 250 gpm, until it was capped two days later.

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the well bore at TD will be:  $(5318) \text{ (ft.) } (.433) \text{ (psi/ft) } = 2302 \text{ psi i.e., more than twice the critical pressure of carbon dioxide.}$

Again, under normal conditions the temperature of the formation at TD can be calculated from depth and the geothermal gradient, usually  $2^{\circ}\text{F}/100 \text{ ft.}$  The initial temperature of the Cabot well would therefore be  $106^{\circ}\text{F}$ , [i.e.,  $(5318)(.02)$ ]. However, the ambient temperature in the wellbore and the fracture system in which the effluents are injected will largely be determined by and will be close to the temperature of the wastes themselves. The latter will vary possibly upwards of  $32^{\circ}\text{F}$  depending on the local weather conditions, if the wastes are stored in open-air holding ponds or storage tanks. And the temperature can be much higher if the wastes are discharged directly into the well from the chemical plant or reactor. Also, the waste emplacement zone temperature near the well bore would, in general, be strongly influenced by the net thermal effects of the formation temperature, and the thermal character of the chemical reaction between the acid and the carbonate formation as well as the heat of dilution of the acid itself.

Under normal operating conditions, the Cabot well received the dilute acid wastes from the holding pond. It is unlikely that the well bore temperature following such injections would have exceeded the critical temperature of carbon dioxide ( $88^{\circ}\text{F}$ ). If the carbon dioxide generated in situ by the chemical reaction between acid and carbonate rock over a given time interval, were in excess of that required to completely

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88°F, the amount of carbon dioxide released will all be in the gaseous ("super-critical gas"), not liquid State. Under appropriate conditions, a rise in temperature therefore can cause an abrupt rise in the borehole pressure with consequences similar to those documented for the 1975 blowout of the Cabot well. A quantitative assessment of the blowout potential of such an operation will require a detailed study of the chemical and thermochemical character of the reactions taking place in the emplacement zone, and the solubility of carbon dioxide in the effluent as a function of effluent temperature and composition (including pH as a major variable). It is to be noted, that the Cabot report on the blowout, emphasizes the concentration of the acid and the solubility of carbon dioxide. It makes no mention of temperature which controls both the solubility of the carbon dioxide and the chemical reactivity of the acid which generates the carbon dioxide.

#### Need to Eliminate Effluent-Formation Interaction

Regardless of whether the Cabot well blowout in August 1975 was on account of the gas pressure build-up or conditions related to the critical properties of carbon dioxide, there is little doubt the primary reason for the incident is the chemical interaction between the acid effluent and the carbonate formation. The latter continues to be a real and unaddressed danger to the safety of waste disposal operations of this type.

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## The Role of the Critical Properties of Carbon Dioxide in Relation to Acid Industrial Waste Disposal in Subsurface Carbonate Formations

### Introduction

There are several facilities in the US which currently dispose of acid wastes by deep well injection into carbonate formations. The chemical reaction between the acid and the carbonate minerals of the emplacement formation which this mode of waste disposal entails, is generally considered to be a favorable feature of the process as the "etching" action of the acid enlarges the disposal zone and possibly increases its transmissivity. However, the operational history of some of these facilities indicates at least two instances of well blow-outs routinely attributed to gas pressure build-up in the well bore. The facilities continue to operate as usual, though the technical cause of the blow-outs and possible measures to pre-empt them in the future still need to be clearly identified. A preliminary examination of the circumstances surrounding one such incident in Illinois appears to suggest that the carbon dioxide produced under normal subsurface conditions is in the liquid state. Eruptions occur when the temperature of the formation exceeds the critical temperature of carbon dioxide (88°F) and the liquid carbon dioxide is transformed into the gaseous form with explosive violence. The role of temperature control on the safety of this mode of waste disposal thus appears to be critical, though not recognized as such by the operators.

### Phase Behavior of Carbon Dioxide.

The theory of the liquifaction of gases as described in standard textbooks of Physics and Chemistry, states that a gas cannot be condensed to its liquid state by compression or increase of pressure alone above a certain limiting temperature known as the "critical temperature". For carbon dioxide, the critical temperature is 88°F. The minimum pressure required to liquify or condense the gas at the critical temperature to the liquid is known as the "critical pressure". The critical pressure of carbon dioxide has been found to be 1070 psia. In practical terms this means that carbon dioxide would exist only in the liquid state as long as its temperature is below 88°F and the pressure above 1070 psia. (At temperatures below 88°F and pressures below 1070 psia it will be technically in the "vapor" form, though it is generally referred to, under these conditions as a "gas").



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## Carbon Dioxide Phase Behavior under Subsurface Conditions

The ensuing discussion relates primarily to the acid waste disposal facility in Illinois, already referred to. The injection well at this facility was completed in the cavernous Eminence-Potosi dolomite formation at a depth of 5318 feet by the Cabot Corporation at its plant facility in Tuscola, IL. The injection well #1, presently a standby, was designed to dispose of hydrochloric acid wastes generated by the Cabot Corporation's chemical plant. Two waste acid streams, one containing about 2% acid and the other about 30 % acid were discharged into the disposal well. The dilute acid stream resulted from the dumping of the concentrated acid from the chemical reactor into a holding pond where it was stored until disposal by well injection. Depending upon the circumstances of plant operation, the injection well also received on occasion or possibly frequently the concentrated and presumably hot acid directly from the chemical reactor.

It thus appears that the temperature of the acid waste could vary from that of the holding pond at the mean atmospheric temperature, say 60°F, to well over 88°F depending on the temperature of the effluent from the chemical reactor. Obviously, the temperature of the injection zone was close to that of the emplaced fluid. It may be mentioned that the temperature at total well depth of the contiguous formation would have an estimated value of 166°F, assuming a mean surface temperature of 66°F and a mean geothermal gradient of 2°F/100 ft. However, the formation temperature cannot have any appreciable influence on the emplacement zone temperature as long as the well remained active. The Cabot well normally accepted fluid at a mean well head pressure of 25 psi (2320 psi, at the sandface at total depth assuming a hydrostatic gradient of 0.433 psi/ft. corresponding with an injection fluid specific gravity of unity). Under normal operating conditions, therefore, the fluid was under a pressure over twice as much as the critical pressure of carbon dioxide. Hence, the temperature of the formation and the resident fluids alone would have determined the physical state of the produced carbon dioxide. Below 88°F, obviously the latter would have been in the liquid state, and remained in that state by the ambient pressure. Liberation of vapor ("gas") could not occur unless the well was pumped to reduce the hydrostatic pressure below 1070 psia, or stated more accurately, below the saturated vapor pressure of carbon dioxide at the injection zone temperature.

While the normal temperature of fluids around the well bore appear to have been close to that of the acid wastes from the holding pond, probably well below 88°F, (else the formation would not have accepted fluid essentially under gravity), continued injection of the concentrated hot acid from the chemical reactor intermittently over a relatively long period could obviously have caused its rise well above 88°F. The transformation of dissolved (liquid) carbon dioxide to the gaseous state when this temperature is

exceeded, would be associated with a build-up of a gas saturation around the well bore and a partial or total loss of the capacity of the well to take in fluid. This, indeed, appears to have happened in August 1975 before the well erupted and ejected a section of the tubing through the well head. From available records it appears that the minimum pressure within the wellbore when the eruption occurred was 2745 psia.

### Conclusions

The documented circumstances and data on the blow-out of the Cabot Corporation well leaves little doubt that the cause of the loss of well capacity followed by the eruption of the well in August 1975, was the result of an increase in the temperature of the emplacement zone and resident fluids above the critical temperature of carbon dioxide (88°F). The warming up of the formation occurred on account of the intermittent injection of the concentrated (and presumably hot) acid directly from the chemical reactor into the injection well. The build-up of a gas pressure could not have occurred at temperatures below 88°F (the critical temperature of carbon dioxide) as theoretical considerations preclude the existence of carbon dioxide under the prevailing subsurface conditions except as a liquid.

The incident emphasizes the need for a closer look at the safety of acid waste disposal in carbonate formations by deep well injection. While the ultimate fate and role of the carbon dioxide formed in the subsurface during such waste disposal cannot be predicted with any degree of certainty, it is quite clear, that the short term safety of the operation requires that the temperature of the emplacement zone and the resident fluids in an active well should be controlled and maintained well below 88°F, the critical temperature of carbon dioxide.

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